(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12379 A1

(51) International Patent Classification[7]: C08J 9/10, B29C 44/10

(21) International Application Number: PCT/GB01/03496

(22) International Filing Date: 2 August 2001 (02.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0019171.8 5 August 2000 (05.08.2000) GB

(71) Applicant (*for all designated States except US*): **ZOTEFOAMS PLC** [GB/GB]; 675 Mitcham Road, Croydon, Surrey CR9 3AL (GB).

(72) Inventor; and
(75) Inventor/Applicant: **WITTEN, Neil** [/]; Zotefoams PLC, 675 Mitcham Road, Croydon.

(74) Agent: **NOVAGRAAF PATENTS LIMITED**; The Crescent, 54 Blossom Street, York YO24 1AP (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

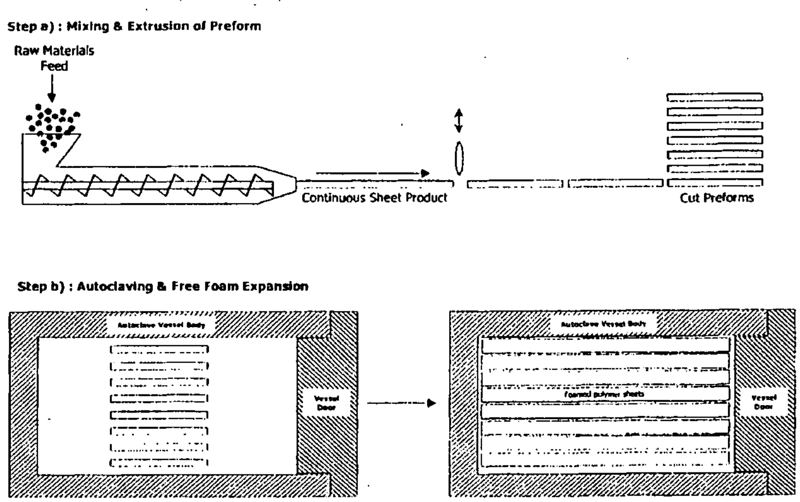
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *with amended claims*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PREPARATION OF CROSS LINKED POLYMER FOAM

Apparatus & Process of the Invention



(57) Abstract: Process for the preparation of a closed cell, cross linked polymer foam comprising in a "single stage expansion": a. Pre-mixing of polymer material, crosslinking agent and chemical blowing agent at a temperature which is insufficient to activate crosslinking and decomposition of the chemical blowing agent; b. [illegible] shaped and sized preform comprising pre-mix (a) in an inert atmosphere in an autoclave and subjecting to elevated temperature to initiate both crosslinking and decomposition of the blowing agent; and c. subsequently subjecting to a rapid pressure reduction, which is sufficient to allow full expansion by the blowing gases released in b) above, apparatus therefor, polymer foam obtained thereby and the use thereof.

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PROCESS FOR THE PREPARATION OF CROSS LINKED POLYMER FOAM

The present invention relates to a process for the preparation of shaped closed cell, cross-linked polymer foam, apparatus for the preparation thereof, shaped closed cell cross-linked polymer foam obtained therewith and the use thereof. More particularly the invention relates to a process for the preparation of shaped closed cell cross-linked polymer foam incorporating the use of foaming agents, the apparatus for the preparation thereof, polymer foam obtained thereby and their use.

It is well established that polymers such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), copolymers of ethylene, styrene butadiene copolymers, polyisoprene and others may be expanded to produce foams by the incorporation of and subsequent reaction by heat of chemical blowing agents, an example of which is Azodicarbonamide (ADCN).

To provide the polymer melt with improved extensional properties and structural stability a crosslinking step is normally employed. Furthermore, the crosslinking step enhances processability by widening the 'foaming' process window and allows a degree of control over cell size in the final product.

A typical process for the manufacture of such foams of density down to 70kg/m^3 comprises a 'single stage' expansion process comprising three steps:

a. Pre-mixing of polymer material, crosslinking agent and chemical blowing agent at a temperature which is insufficient to activate crosslinking and/or blowing agent decomposition;

b. transfer of 'slugs' of the pre-mixed material to a mould, in a heated press and heating to initiate both cross-linking and release of the expansion gases through blowing agent decomposition;

c. press opening with subsequent material expansion. Expansion occurs as a result of pressure exerted by the released gas(es) on the hot polymer causing expansion out of the mould. The block foam is then cooled and removed.

To produce foams of density significantly lower than $70kg/m^3$, greater control of the blowing agent decomposition and foam expansion must be achieved and expansion is normally carried out in a second, larger mould in one of two ways, referred to as a 'two-stage expansion' process, following

steps a-c above and additionally

in step b: only partial release of expansion gases, through blowing agent decomposition prior to

bi. transfer to a larger mould, further heating and release of expansion gases or,

in step b. decomposition of blowing agent, and cooling to prevent full expansion prior to

bii transfer of unexpanded 'slug' to a second large mould for re-heating and subsequent full expansion.

Both the 'single' and 'two stage expansion' processes suffer however from residual core heat retention which leads to a wide density variation through the thickness in the final foam product.

A common and essential feature of all these processes is the mould and press as a means of defining and controlling the shape of the final product. Expansion is restrained due to these features leading to a product with wide density variations, cell structure variations and in-built stresses.

The prior art processes are inconvenient in terms of the 'two stage expansion', costly in terms of additional equipment required and time required to occupy first and second stage moulds during expansion, complex in terms of need to monitor conditions. Accordingly there is a need for a more convenient process for the production of closed cell, cross-linked cellular polymers.

We have now surprisingly found that a single stage process may be employed for preparation of foams, with use of temperature to initiate decomposition and applied gas pressure to control the polymer expansion.

In its broadest aspect there is provided according to the present invention a process for the preparation of a closed cell, cross linked polymer foam comprising in a 'single stage expansion':

a. Pre-mixing of polymer material, crosslinking agent and chemical blowing agent at a temperature which is insufficient to activate crosslinking and decomposition of the chemical blowing agent;

b. providing at least one shaped and sized preform comprising pre-mix (a) in an inert atmosphere in an autoclave and subjecting to elevated

temperature to initiate both crosslinking and decomposition of the blowing agent; and

c. subsequently subjecting to a rapid pressure reduction, which is sufficient to allow full expansion by the blowing gases released in b) above.

The process of the invention enables controlled expansion to produce a high quality foam, without the need to use multiple moulds or presses. It is a particular advantage of the invention that controlled expansion is substantially isotropic and serves to reduce in-built stresses, with substantially uniform product properties throughout the product.

This has the further advantage that foams obtained post production have dimensional stability whereby dimensional changes, i.e. distortions, are minimised.

Reference herein to an autoclave is to any vessel allowing control of pressure and temperature of the contents thereof.

The process may be employed for the preparation of any desired forms, and is best suited for the preparation of regular forms such as tiles, sheets and other essentially planar products. Size of preforms is suitably selected by anticipation of the subsequent isotropic expansion.

It is a particular advantage of the invention that mixing and shaping may be carried out by known techniques, for example with use of a compounding extruder with a profiled thick sheet die, and subsequently cutting to required dimensions; or with use of internal mixers, mills etc., and a light press and

mould. Preferably preforming is via the extrusion method which allows continuous production, improved mix quality and control of foam sheet thicknesses.

The process may be used for the preparation of any foamed polymers which are capable of being processed (melted) below the decomposition temperature of the corresponding blowing agent and which enable additive mixing before foaming and crosslinking. It is an advantage that the initiation of the crosslinking reaction serves to maintain preform shape prior to and during decomposition of the chemical blowing agent, whereby controlled expansion is possible.

The process is particularly suited for the preparation of known and novel olefinic polymers. Known polymers are selected from low density polyethylene (LDPE), such as elastomeric polyethylene or EPDM and elastomeric or plastomeric metallocene polyethylene, and copolymers thereof such as ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA), ethylene methyl acrylate (EMA) and the like. It is within the scope of this invention that the process is suited for preparing foams from novel olefinic polymers and polymer blends which are continuously being developed and made commercially available.

Most preferably the process is suited for the preparation of polymers having sufficient melt strength to form and maintain a cellular structure on release of blowing agent and to retain their preform shape at temperatures in excess of or equal to 165°C. Melt strength may be controlled by selection of polymer rheological properties, and/or nature or amount of crosslinking agent

Any crosslinking agent may be employed which is compatible with the polymer. Preferred crosslinking agent comprises a high temperature decomposition peroxide. Peroxides commonly employed are those of the diarylalkyl peroxide class, such as dicumyl peroxide or α.ά - bis(tert-butylperoxy) disopropylbenzene. The crosslinking agent is selected in nature and amount to give sufficient cohesion to provide melt stability during blowing agent decomposition at elevated temperature.

Any known blowing agent may be employed which is compatible with the selected polymer as powder or master batch (granule preblend) and releases sufficient gas to achieve desired foaming and density reduction. Conventional chemical blowing agents such as azodicarbonamide (ADCN) are preferred for generating gases within the polymer

In the premix step any additional agents may be added such as activator, solvent, heat transfer materials, such as refractory materials and inorganic oxides, lubricant, filler, pigment and the like as known in the art.

The inert atmosphere in the autoclave is suitably provided by known means to prevent oxidation and avoid fire hazard, and preferably comprises a nitrogen, argon or like atmosphere.

Heating of the polymer formulation in the step (b) may be by any suitable means and is preferably convective heating by heat of gases in the autoclave. Heating is to a temperature in the range 80-250°C, depending on the nature of the polymer, crosslinking agent and blowing agent, sufficient to initiate crosslinking with subsequent decomposition of the chemical blowing agent.

In a preferred embodiment of the invention the process comprises preparation of a closed cell crosslinked polymer foam according to steps a-c as hereinbefore defined of a polymer having melt temperature in a first range Tm, comprising

in step a) pre-mixing the polymer with a crosslinking agent having activation temperature in a second range Ta and a chemical blowing agent having decomposition temperature in a third range Tb, wherein temperature ranges are in increasing or overlapping order Tm < Ta < Tb; and

in step b) heating of at least one shaped preform at a rate whereby initial polymer melt takes place partially or completely, followed by partial or complete activation of crosslinking agent, followed by partial or complete decomposition of chemical blowing agent.

Suitable temperature ramping may be selected as known in the art, for example uniform or otherwise. Rate of temperature increase and final temperature achieve control of concentration and yield of released gases, uniformity and degree of crosslinking and the like. Rate of temperature increase may be determined by those skilled in the art with reference to size of preforms, efficiency of heat uptake in any given autoclave, nature of polymer, crosslinking agent and blowing agent, desired polymer foam density, (and therefore amount of blowing agent), desired degree of crosslinking and the like. Suitable temperature increase is of the order of 1°C/minute - 5°C/minute.

Pressure in step b) may be ambient or elevated. Elevated pressure may be applied by any known means suitable with use of autoclaves and is preferably by elevating surrounding gas pressure in the sealed autoclave. It is a particular

advantage of the invention that pressure control is uniform about and throughout the polymer, during heating.

Pressure in step c) is rapidly reduced to atmospheric. It is a further advantage that an autoclave permits a rapid release of pressure with isotropic expansion in simple and effective manner. Suitably elevated pressure in step (b) is applied in the range up to 25 bar. Pressure reduction in step c) may be at any convenient rate, and may be only constrained by the limitations of valve apertures of a given autoclave allowing gas release.

In a further aspect of the invention there is provided an apparatus for the preparation of shaped closed cell crosslinked polymer foam as hereinbefore defined comprising in line a mixer, means for shaping polymer premix into preforms, and an autoclave for subjecting to elevated temperature and pressure, with means for regulation thereof.

In a further aspect of the invention there is provided a closed cell crosslinked polymer foam or precursor thereof obtained with use of the process or apparatus of the invention as hereinbefore defined. Polymer may be of any desired size and form, preferably in the form of tiles or sheets as hereinbefore defined. Final required foam size is restricted only by size constraint of apparatus used.

In a further aspect of the invention there is provided the use of a closed cell crosslinked polymer foam obtained with the process of the invention as hereinbefore defined for (thermal) insulation, flooring, lining and the like in lightweight or structural applications such as aerospace, automotive, packaging, sports, leisure and toy industries, building or industrial applications, for use in gasketting or in medical applications and the like.

The invention is now illustrated in non-limiting manner with reference to the following figures and examples wherein

Figure 1 illustrates a conventional apparatus and process;

Figure 2 illustrates the apparatus and process of the invention.

Figure 3 illustrates a suitable temperature/time profile for step b) of the invention.

In Figure 1 the apparatus comprises means for mixing and shaping polymer and sets of moulds contained polymer for processing. It will be appreciated that the additional work required in the two stage process for transferring polymer from a mould to a second mould or to an oven is cumbersome and requires additional manpower or automation.

In Figure 2 is illustrated a premixing and extrusion apparatus, in line with an autoclave. The use of moulds is not required and preformed polymer is simply stacked onto shelves for processing. Processing is rapid allowing efficient batchwise production of high quality polymer foam.

It is within the scope of the invention to isolate a foamable polymer precursor for storage with subsequent foaming, whereby for example extruded or a shaped premix preforms may be manufactured according to step a). It is an advantage that intermediate preforms may be foamed locally according to step c) of the process of the invention, with use of minimal equipment in the form of a simple autoclave or the like. Blending and shaping apparatus such as extrusion apparatus may therefore be employed centrally.

Example 1

A formulation consisting of polymer granules, crosslinking agent and chemical blowing agent were blended and fed continuously to an extrusion hopper in the following proportions:

Material	Function	Grade & Supplier	Proportion (%)
Ethylene Vinyl Acetate resin	Base polymer resin	Greenflex ML50 [Polimeri Europa S.A.]	96.6
α,ά-bis(tert-butylperoxy) diisopropylbenzene	Crosslinking agent	Vulcup-R [Hercules Ltd]	0.7
Azodicarbonamide	Chemical Blowing Agent	Genitron KA9183 [Bayer plc]	2.7

The materials were mixed at temperature in the range 110°C to 125°C to form a melt which was extruded at a controlled output rate to produce a homogeneous, continuous sheet. The sheet was allowed to self-cool due to the low linear speed giving an evenly crystallised sheet product and so minimising internal stress. The cooled sheet was sectioned into pre-defined blocks and subsequently stacked onto supporting shelves of an autoclave.

The autoclave operates batch-wise and can contain any number of sheets, being constrained only by the size and design of the vessel. In this example twenty-one sheets were simultaneously expanded into foam.

Initially the vessel was evacuated and filled with nitrogen gas. The gas pressure was then increased from atmospheric to 20 bar at a rate of 19 bar per minute, i.e. for one minute. Simultaneously, the temperature of the gas within the autoclave was increased at a rate of 3°C per minute up to 200°C.

After a further period of 45 minutes, the gas pressure was released rapidly, subject only to the constraints of the apparatus. On full pressure release the foamed blocks were removed from the autoclave and allowed to cool at ambient temperature and pressure.

Further advantages of the invention are apparent from the foregoing.

CLAIMS

1. Process for the preparation of a closed cell, cross linked polymer foam comprising in a 'single stage expansion':

a. Pre-mixing of polymer material, crosslinking agent and chemical blowing agent at a temperature which is insufficient to activate crosslinking and decomposition of the chemical blowing agent;

b. providing at least one shaped and sized preform comprising pre-mix (a) in an inert atmosphere in an autoclave and subjecting to elevated temperature to initiate both crosslinking and decomposition of the blowing agent; and

c. subsequently subjecting to a rapid pressure reduction, which is sufficient to allow full expansion by the blowing gases released in b) above.

2. Process as claimed in Claim 1 wherein expansion is controlled and is substantially isotropic.

3. Process as claimed in any of Claims 1 and 2 for the preparation of regular forms such as tiles, sheets and other essentially planar products.

4. Process as claimed in any of Claims 1 to 3 wherein size of preforms is selected by anticipation of the subsequent isotropic expansion.

5. Process as claimed in any of Claims 1 to 4 wherein mixing and shaping

is carried out with use of a compounding extruder with a profiled thick sheet die, and subsequently cutting to required dimensions; or with use of internal mixers, mills etc., and a light press and mould.

6. Process as claimed in any of Claims 1 to 5 wherein preforming is via the extrusion method which allows continuous production, improved mix quality and control of foam sheet thicknesses.

7. Process as claimed in any of Claims 1 to 6 for the preparation of polymers selected from low density polyethylene (LDPE), such as elastomeric polyethylene or EPDM and elastomeric or plastomeric metallocene polyethylene, and copolymers thereof such as ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA) and ethylene methyl acrylate (EMA).

8. Process as claimed in any of Claims 1 to 7 wherein a crosslinking agent comprises a high temperature decomposition peroxide.

9. Process as claimed in any of Claims 1 to 8 wherein a blowing agent comprising azodicarbonamide (ADCN) is used for generating gases within the polymer

10. Process as claimed in any of Claims 1 to 9 wherein heating of the polymer formulation in the step (b) is to a temperature in the range 80-250°C sufficient to initiate crosslinking with subsequent decomposition of the chemical blowing agent.

11. Process as claimed in any of Claims 1 to 10 for preparing a polymer having melt temperature in a first range Tm, comprising

in step a) pre-mixing the polymer with a crosslinking agent having activation temperature in a second range Ta and a chemical blowing agent having decomposition temperature in a third range Tb, wherein temperature ranges are in increasing or overlapping order Tm < Ta < Tb; and

in step b) heating of at least one shaped preform at a rate whereby initial polymer melt takes place partially or completely, followed by partial or complete activation of crosslinking agent, followed by partial or complete decomposition of chemical blowing agent.

12. Process as claimed in any of Claims 1 to 11 wherein elevated pressure in step (b) is applied in the range up to 25 bar.

13. Apparatus for the preparation of shaped closed cell crosslinked polymer foam as hereinbefore defined in any of Claims 1 to 12 comprising in line a mixer, means for shaping polymer premix into preforms, and an autoclave for subjecting to elevated temperature and pressure, with means for regulation thereof.

14. Closed cell crosslinked polymer foam or precursor thereof obtained with use of the process or apparatus of the invention as hereinbefore defined in any of Claims 1 to 13.

15. The use of a closed cell crosslinked polymer foam obtained with the process of the invention as hereinbefore defined for (thermal) insulation, flooring, lining and the like in lightweight or structural applications such as aerospace, automotive, packaging, sports, leisure and toy industries, building or industrial applications or for use in gasketting or in medical applications.

AMENDED CLAIMS
[received by the International Bureau on 10 January 2002 (10.01.02);
original claims 1-15 replaced by amended claims 1-14 (3 pages)]

1. Process for the preparation of a closed cell, cross linked polymer foam comprising in a 'single stage expansion':

a. Pre-mixing of polymer material having melt temperature in a first range Tm, crosslinking agent agent having activation temperature in a second range Ta and a chemical blowing agent having decomposition temperature in a third range Tb, at a temperature which is insufficient to activate crosslinking and decomposition of the chemical blowing agent, wherein temperature ranges are in increasing or overlapping order Tm < Ta < Tb;

b. providing at least one shaped and sized preform comprising pre-mix (a) in an inert atmosphere in an autoclave at elevated pressure and heating at a rate whereby initial polymer melt takes place partially or completely, followed by partial or complete activation of crosslinking agent, followed by partial or complete decomposition of chemical blowing agent; and

c. subsequently subjecting to a rapid pressure reduction, which is sufficient to allow full expansion by the blowing gases released in b) above.

2. Process as claimed in Claim 1 wherein rate of heating in step b) is of the order of 1°C per minute - 5°C per minute.

3. Process as claimed in any of Claims 1 to 2 for the preparation of regular forms such as tiles, sheets and other essentially planar products.

4. Process as claimed in any of Claims 1 to 3 wherein size of preforms is selected by anticipation of the subsequent isotropic expansion.

5. Process as claimed in any of Claims 1 to 4 wherein mixing and shaping is carried out with use of a compounding extruder with a profiled thick sheet die, and subsequently cutting to required dimensions; or with use of internal mixers, mills etc., and a light press and mould.

6. Process as claimed in any of Claims 1 to 5 wherein preforming is via the extrusion method which allows continuous production, improved mix quality and control of foam sheet thicknesses.

7. Process as claimed in any of Claims 1 to 6 for the preparation of polymers selected from low density polyethylene (LDPE), such as elastomeric polyethylene or EPDM and elastomeric or plastomeric metallocene polyethylene, and copolymers thereof such as ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA) and ethylene methyl acrylate (EMA), and blends thereof.

8. Process as claimed in any of Claims 1 to 7 wherein a crosslinking agent comprises a high temperature decomposition peroxide.

9. Process as claimed in any of Claims 1 to 10 wherein a blowing agent comprising azodicarbonamide (ADCN) is used for generating gases within the polymer

10. Process as claimed in any of Claims 1 to 9 wherein heating of the polymer formulation in the step (b) is to a temperature in the range 80-250°C sufficient to initiate crosslinking with subsequent decomposition of the chemical blowing agent.

11. Process as claimed in any of Claims 1 to 10 wherein elevated pressure in step (b) is applied in the range up to 25 bar.

12. Apparatus for the preparation of shaped closed cell crosslinked polymer foam as hereinbefore defined in any of Claims 1 to 11 comprising in line a mixer, means for shaping polymer premix into preforms, and an autoclave for subjecting to elevated temperature and pressure, with means for regulation thereof.

13. Closed cell crosslinked polymer foam or precursor thereof obtained with use of the process or apparatus of the invention as hereinbefore defined in any of Claims 1 to 12.

14. The use of a closed cell crosslinked polymer foam obtained with the process of the invention as hereinbefore defined in any of Claims 1 to 11 for (thermal) insulation, flooring, lining and the like in lightweight or structural applications such as aerospace, automotive, packaging, sports, leisure and toy industries, building or industrial applications or for use in gasketting or in medical applications.

STATEMENT UNDER ARTICLE 19

Claim 1 is amended in view of the cited documents to more clearly indicate the feature of controlled expansion of polymer, as described at page 7 lines 16 to 19, using substrates having increasing or overlapping temperatures as defined in Claim 11. This is clearly distinct from the cited documents, as indicated in the Search Report. Claim 1 is also amended with reference to page 7 line 26 specifying elevated pressure.

A preferred embodiment of the control feature of Claim 1 is indicated in new Claim 2 which takes basis from the description at page 7 line 24.

Claim 7 is amended with reference to page 5 line 20 to specify known blends of polymers.

The remaining claims as originally filed are renumbered.

Figure 1 : Illustration of Conventional Apparatus & Process

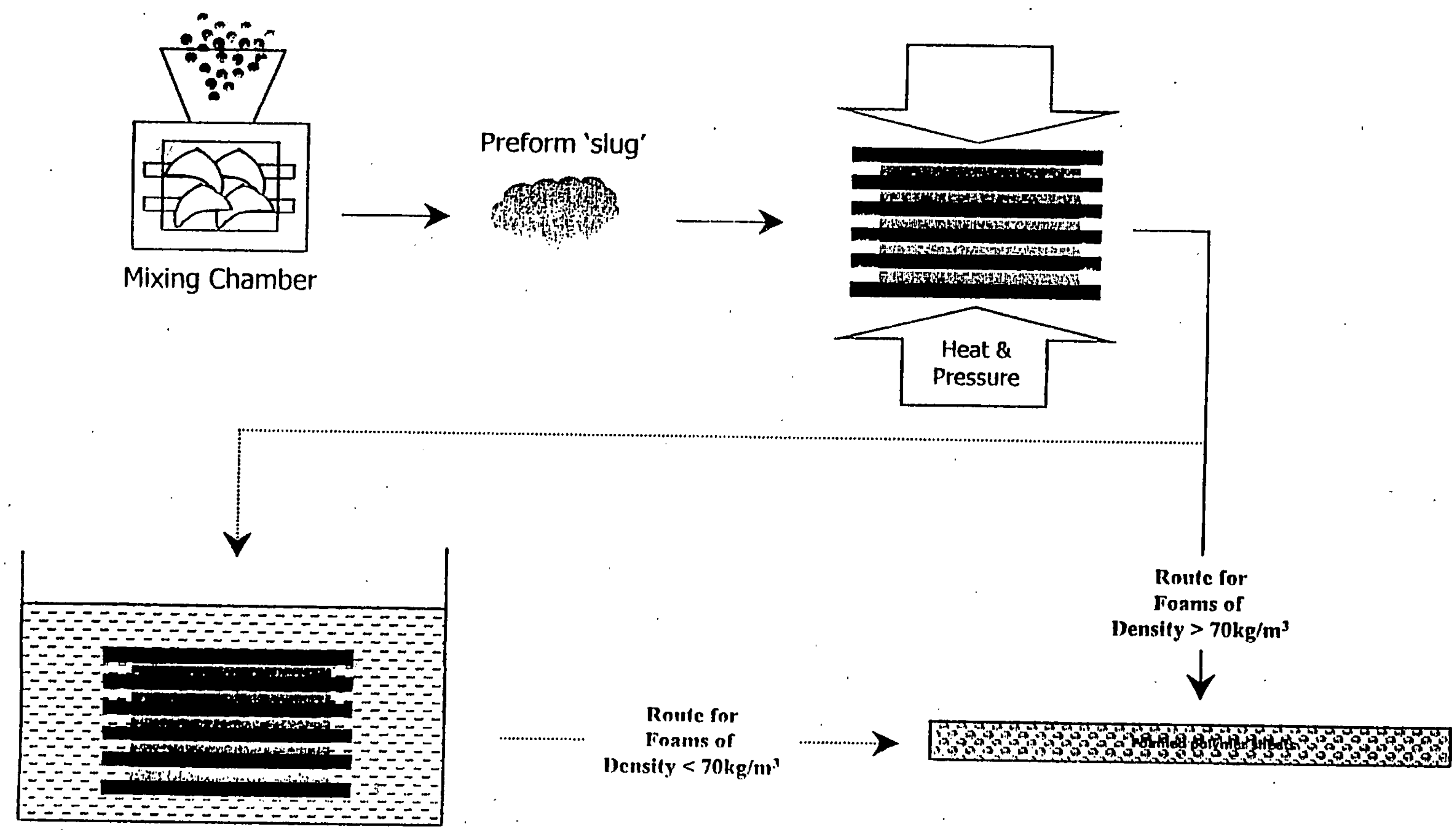
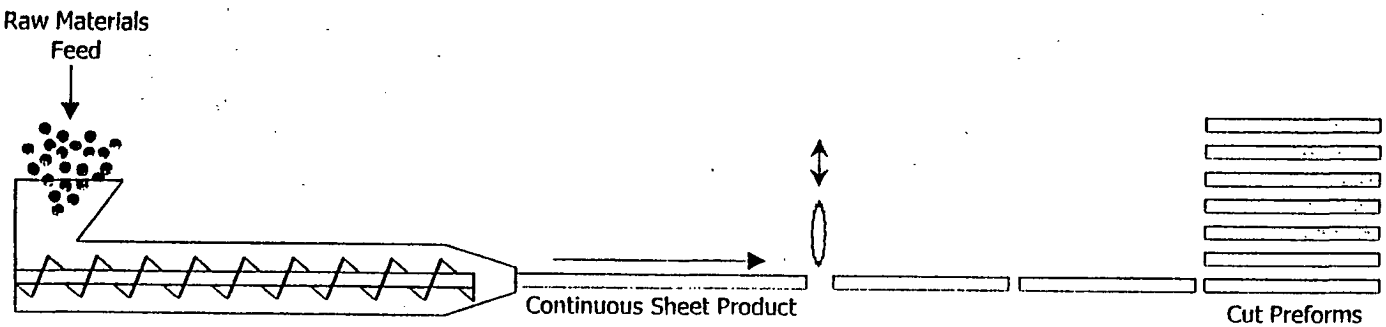
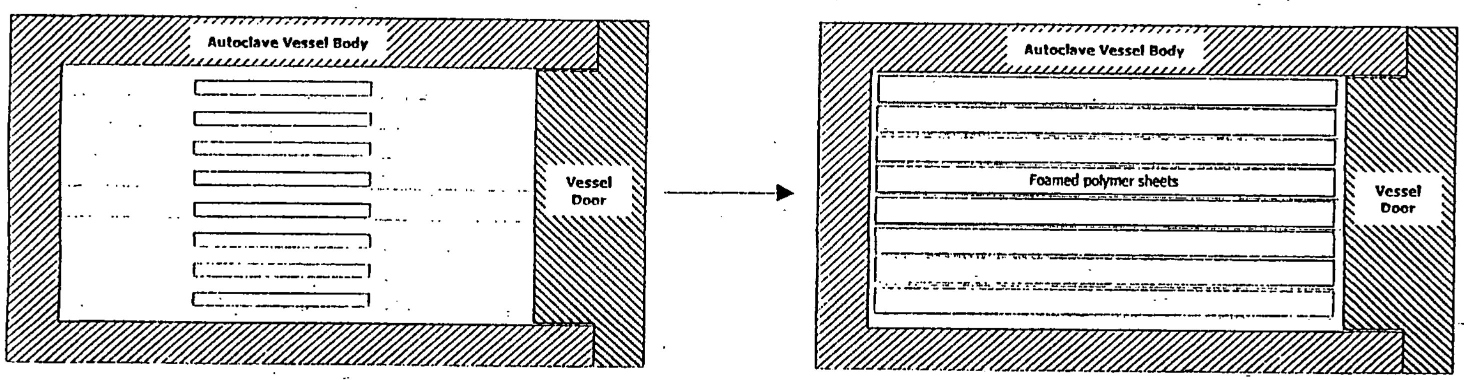


Figure 2 : Apparatus & Process of the Invention

Step a) : Mixing & Extrusion of Preform



Step b) : Autoclaving & Free Foam Expansion



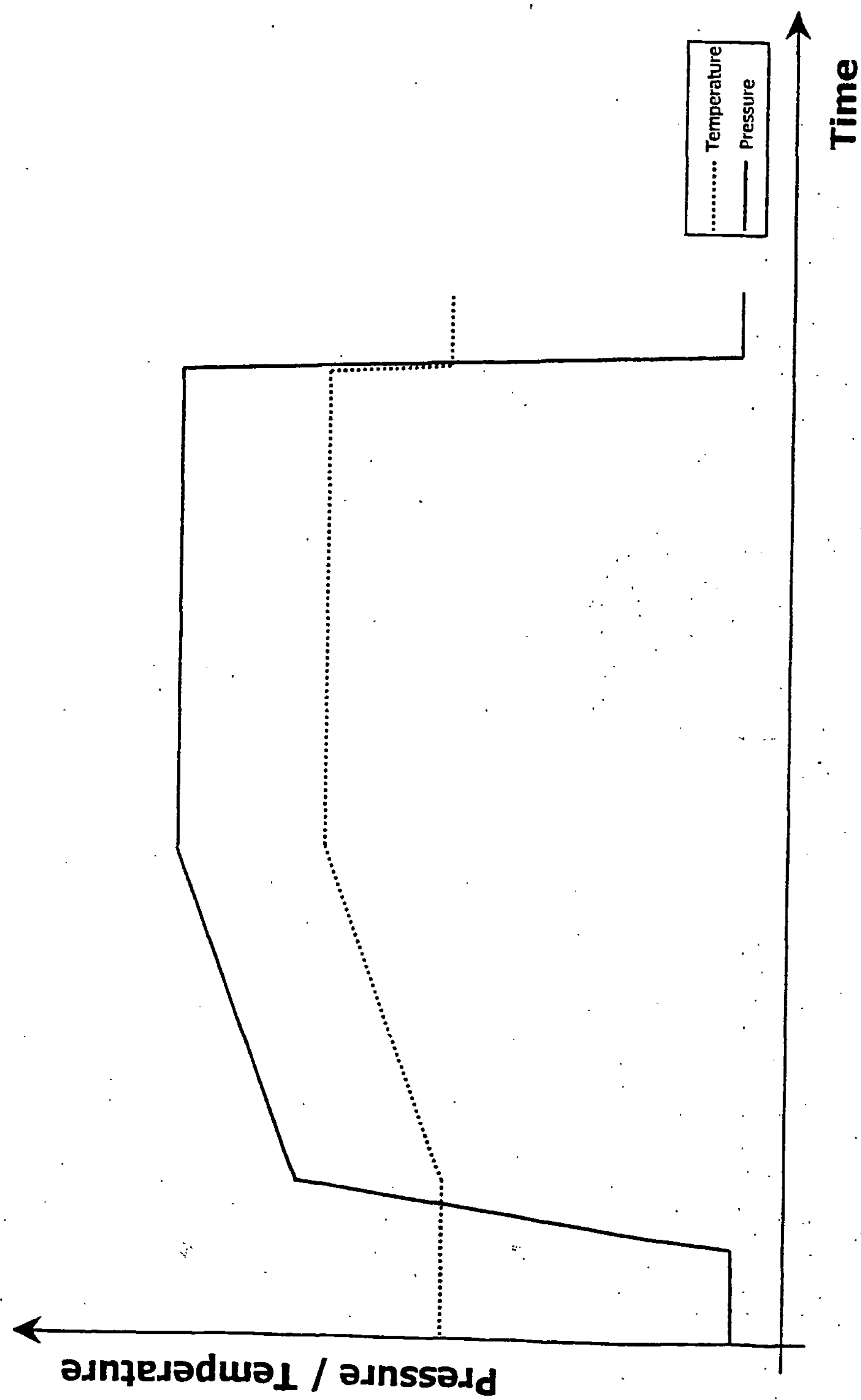


Figure 3 : Temperature/Pressure/Time Profile In Step b) of the Invention

INTERNATIONAL SEARCH REPORT

Intei nal Application No
PC1/GB 01/03496

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/10 B29C44/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 559 190 A (QUINTAVALLE SAVERIO ET AL) 17 December 1985 (1985-12-17) examples column 4, line 41-52 claims	1-10, 13-15
X	DATABASE WPI Section Ch, Week 198142 Derwent Publications Ltd., London, GB; Class A32, AN 1981-76667D XP002182217 & JP 56 111658 A (TOYO RUBBER CHEM IND CO), 3 September 1981 (1981-09-03) abstract	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 November 2001	20/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk [illegible] Fax: (+31-70) 340-3016	Oudot, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter ıal Application No
PCT/GB 01/03496

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